(12) UK Patent Application (19) GB (11) 2 082 976 A

(21) Application No 8124709
(22) Date of filing 12 Aug 1981
(30) Priority data
(31) 55/114989
(32) 20 Aug 1980
(33) Japan (JP)
(43) Application published
17 Mar 1982
(51) INT CL³
B41C 1/10
(52) Domestic classification
B6J 707 MF
B6C 602 630 631 635
636 637 643 644 HD
(56) Documents cited
GB 1544196
GB 1320785
GB 1265597
GB 1149759
GB 1063007
(58) Field of search
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B6J
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(54) **Printing Plate Manufacture**

(57) A method for the production of a printing plate is provided which comprises forming a printing ink image on a resin layer provided on a printing plate material, and dissolving the resin layer with a solvent therefor which does not dissolve the inked image.

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SPECIFICATION

Method for the Production of a Printing Plate

The present invention relates to a method for the production of printing plates, and more particularly to a method for the production of printing plates which has improved operability adapted for the duplication of printing plates, with the capability of withstanding the printing of a larger number of copies.

A general method for obtaining offset printing plates involves preparing a negative or positive film, which thereafter is brought into contact with a negative type presensitized plate (hereinafter referred to as a "P.S. plate") or a position type P.S. plate to be subjected to imagewise exposure and then processed in a given developer solution, whereby the non-image area is dissolved and removed. However, the reality has been such that the method, because it involves the preparation of a film, exposure to light of a P.S. plate through the film and the development of the P.S. plate, is inevitably uneconomic because of the time and costs involved in the production of a plurality of printing plates. Besides, today, electronic editing systems are a practical reality even in the news printing field owing to extensive and diversified applications of computers, such that a method of writing electric-signal image information on a film or a printing plate material by means of a laser beam has been used. The system for recording on a film by means of a laser beam, because it includes procedures for film development and exposure of the P.S. plate to light, is slower than the direct plate making system. At present, the direct plate making system wherein exposure is made on a printing plate material directly by means of a laser beam may be the best way for rapidly producing printing plates. The direct plate making system has now been commercialized by ECOM Inc and LogEtronic Inc, whose products are capable of making printing plates without the step of preparing any negatives. However, in preparing a plurality of printing plates, the procedure for writing in each of the printing plates by means of a laser beam has problems as regards speed and cost because it requires a scanning time of tens of seconds per page of A2 size, the life of the laser tube is limited, and it is necessary to use printing plate materials which are sensitive to a laser beam. There is therefore a longstanding problem in the trade of mass printing of how to rapidly and inexpensively produce a pluralityof duplicate plates from a printing plate prepared by laser recording.

As for the production of the duplicate plate, Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 100005/1978 describes a method for making printing plates comprising the formation of an ink receptive layer through the offset printing procedure on an aluminium plate subjected to anodic oxidation (hereinafter referred to as A.D. treatment), and further Japanese Patent O.P.I. Publication No. 46973/1980 described a method for making a plurality of printing plates comprising obtaining lithographic plates for mass printing by duplicate-printing with the use of a master plate prepared by means of laser beam recording. These methods reproduce lithographic plates in the manner of offset-printing forming an image using a special ink on a printing plate material in sheet form such as an aluminium plate, in which methods the ink printed on the aluminium plate is used as the component of the duplicate plate for printing. Generally, offset lithographic printing is based on the principle that when the surface of a printing plate, after the non-image area thereof is wetted with water, is given an oily ink, the wetted non-image area repells the oily ink, so that the ink adheres to the oleophilic image area only. To retain an accurate reproduction and homogeneity of the printing image, the balance between the ink and water wetting must be well controlled at the time of printing. Insufficient supply of wetting water or excessive supply of the ink will cause such troubles in the reproduction of a printing image as ink stain on the non-image area, elimination of details, and the dot gain phenomenon when printing using dots. In the duplicate plate having these inked areas as the oleophilic areas thereof, the bonding strength between the ink component formed on the aluminum plate and the aluminum plate itself, the wear-resistance of the ink compositions and the applied quantity of the ink exert a large influence upon the press life of the duplicate plate. However, an increase in the amount of the ink to prolong the press life of the duplicate plate has an adverse effect upon the accurate reproduction of an image as stated above.

This drawback which means that one cannot allow build-up of much ink on the duplicate plate is not only true in the case of offset printing but is also true in the case where duplicate plates are produced from a relief printing master plate. In the relief printing process, if a large amount of ink is built up, the ink squeezes out above the periphery of the relieved portion, resulting in a deterioration in the reproduction image quality.

The aluminum plate for use in making a plurality of printing plates, when not treated to be made hydrophilic, is highly oleophilic, and if some oleophilic material is attached to or fingerprints are left on the plate, then this portion of the plate is subject to deposit of ink, thus sometimes causing a stain. The holes on the surface of the aluminum plate subjected to an A.D. treatment are active, and, when left in the air, may sometimes change with the passage of time, so that the plate becomes unstable when used as a printing plate. When the plate has some flaws on the surface thereof, the flaw may cause troubles in image reproduction. Therefore, operators are compelled to pay careful attention to the aluminum plate during handling.

It is an object of the present invention to provide a method for the production of a printing plate suitable for preparing a plurality of duplicate

lithographic printing plates, and also to provide a method for duplicating, by printing, lithographic printing plates having a longer press life and improved image reproducibility as well as operability.

The present invention provides a method for producing a printing plate whereby an image of a printing ink is provided on a resin layer of a printing plate material, and the resin layer is dissolved in the portion where the image of the printing ink is not formed, with a solvent for the resin.

Printing plate materials usable in the present invention include paper laminated with plastic materials such as polyethylene, polypropylene and polystyrene; plates of metals such as aluminum (including aluminum alloys), zinc, chromium and copper; plastic films such a cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate and polyvinyl acetal; and papers or plastic films laminated or vacuum evaporation-coated thereon with the foregoing metals. Of these materials, an aluminum plate is preferred because of its high dimensional stability as well as its inexpensiveness. Another suitable material is a composite sheet such as a polyethylene terephthalate film laminated to an aluminum sheet, described in e.g. Japanese Patent Examined Publication No. 18327/1973.

The printing plate material used in the present invention, prior to being provided thereon with a resin layer, may be subjected to an appropriate surface treatment. For example, in the case of a support having a plastics surface, the support may be subjected to chemical treatment, discharge treatment, flame treatment, ultraviolet rays treatment, high frequency treatment, glow discharge treatment, active plasma treatment or laser treatment.

One of the most preferred printing plate materials used in the present invention is one having a surface made of aluminum (including aluminum alloys) subjected to a mechanical graining treatment such as ball graining, sandblasting or brush graining; a graining-dressing treatment by chemical graining or electrolytic graining; a dipping treatment using an aqueous solution of e.g. sodium silicate, potassium fluorozirconate or phosphoric acid salts; or a surface treatment such as anodic oxidation. As described in US Patent No. 2,714,066 there may also be used an aluminum plate which, after being subjected to graining treatment and then A.D. treatment, is dipped in an aqueous sodium silicate solution. The said A.D. treatment is carried out by, e.g. the application of an electric current through an aluminum plate as an anode in an electrolyte prepared with one or two or more organic acids such as oxalic acid or sulfamic acid or an aqueous or non-aqueous solution of these acids.

The resin layer provided on the printing plate material used in the present invention should be one that is removable by a solvent except for the image-formed covered with a printing ink, and should possess excellent adherence to the printing plate.

A resin for use in the formation of such a resin layer, whether water-insoluble or water-soluble, should become water-insoluble by, for example, photopolymerization at least during the subsequent printing operation, and should be selected from those soluble in a solvent which does not etch the resist layer made by the coating of the printing ink used in the present invention.

Such resins include, for example, acrylic acid homo- or copolymers, as well as homo-, co-, ter- or higher polymers derived from one or more of: N-(4-hydroxy-phenyl)acrylamide, N-(4-hydroxy-phenyl)methacrylamide, N-(4-hydroxynaphthyl)methacrylamide, o-, m-, p-hydroxy styrene, o-, m-, or p-hydroxy-phenyl methacrylate; α-β unsaturated carboxylic acids and anhydrides such as acrylic acid, methacrylic acid and maleic anhydride; alkyl acrylates such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, octyl acrylate, 2-chloroethyl acrylate, 2-hydroxy-ethyl-acrylate, glycidyl acrylate and N-dimethylaminoethyl acrylate; alkyl methacylates such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, amyl methacrylate, cyclohexyl methacrylate, 2-hydroxy-ethyl methacrylate, 4-hydroxy-butyl methacrylate, glycyl methacrylate and N-dimethyl-aminoethyl methacrylate; acrylamides or methacrylamides such as acrylamide, methacrylamide, N-methylol acrylamide, N-methylol methacrylamide, N-ethyl acrylamide, N-hexyl methacrylamide, N-cyclohexyl acrylamide, N-hydroxy-ethyl acrylamide,N-phenyl acrylamide, N-nitrophenyl acrylamide and N-ethyl, N-phenyl acrylamide; ethylvinyl ether, 2-chloroethyl-vinyl ether, hydroxy-ethyl-vinyl ether, propyl-vinyl ether, butyl-vinyl ether, octyl-vinyl ether, phenyl-vinyl ethers; vinyl esters such as vinyl acetate, vinyl chloroacetate, vinyl butyrate and vinyl benzoate; styrenes such as styrene, α-methyl styrene, methyl styrene and chloromethyl styrene; vinyl ketones such as methyl-vinyl ketone, ethyl-vinyl ketone, propyl-vinyl ketone and phenyl-vinyl ketone; olefins such as ethylene, propylene, isobutylene, butadiene and isoprene; n-vinyl pyrolidone, N-vinyl carbazole, 4-vinyl pyridine, acrylonitrile and methacrylonitrile; p-substituted phenol formaldehyde resins (such as p-t-butyl phenyl formaldehyde resin), m-cresol formaldehyde novolak resins, methacrylic acid copolymers, acrylamide copolymers, methacrylamide copolymers, vinyl pyrolidone copolymers, shellac, epoxy resins, polyamide resins, polyurethane resins and urea resins. Resins usable in the present invention may be selected from these resins, but are not necessarily limited thereto. The resin layer provided on the printing plate in the present invention should contain some of such resins as described above, and aside

from them, may contain, for example, a plasticizer, coloring agent and surfactant.

The resin layer in the present invention is allowed to become a resin layer having a matrix structure by being coated with an emulsion whose dispersoid including, for example, vinyl acetate-ethylene copolymer, poly (methyl acrylate), poly (ethyl acrylate), polyacrylonitrile, polyvinyl acetate, diacetone acrylamide-methyl acrylate copolymer, diacetone acrylamide-acrylonitrile copolymer, diacetone acrylamide-vinyl acetate copolymer, methyl acrylate-vinyl acetate copolymer, methyl acrylate-vinyl chloride copolymer, methyl acrylate-styrene copolymer, ethylene-methacrylic acid copolymer, acrylonitrile-butadiene copolymer or acrylonitrile-styrene copolymer. The mean particle diameter of the matrix material is desirably not more than 15μ. The emulsion may optionally contain a protective colloid, surface active agent, plasticizer or coloring agent for example.

The plasticizer can be necessary to provide the desired plasticity for the resin layer, said plasticizer being, for example, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, diisobutyl phthalate, dioctyl phthalate, octyl-captyl phthalate, dicyclohexyl phthalate, ditridecyl phthalate, butyl-benzyl phthalate, diisodecyl phthalate, diaryl phthalate; a glycol ester such as ethyl-phthalyl-ethyl glycolate, butyl-phthalyl-butyl glycolate or triethylene-glycol-dicaprylic acid ester; a phosphate such as tricresyl phosphate or triphenyl phosphate; an aliphatic dibasic acid ester such as diisobutyl adipate, dioctyl adipate, dimethyl sebacate, dibutyl sebacate, dioctyl azelate, or dibutyl fumarate; polyglycidyl methacrylate, trimethyl citrate, glycerol-triacetyl ester or butyl laurate.

The aforesaid surface active agent improves the removability of the non-image area of the resin layer during development and assists uniform coating of the resin layer on the printing plate. However, the addition of an excessive amount of the agent should be avoided because it will generally have a bad effect upon the press life of the printing plate. The agent can be an anionic surfactant, cationic surfactant nonionic surfactant or amphoteric surfactant; fluorinated surfactants can be used.

The aforementioned coloring agent is useful for judging the removability of the non-image area of the resin layer during the etching treatment, the said coloring agent being generally an organic or inorganic dye or pigment such as an acridine dye, merocyanine dye, cyanine dye, styryl dye, triphenyl methane dye, copper phthalocyanine dye, carbon black, titanium oxide or a quinone imino dye.

As the resin layer in the present invention, conventional negative type photosensitive resin compositions may be used. Therefore, commonly used lithographic negative type P.S. plates may be used as the printing plate of the present invention having a resin layer on the plate material. In such a case, an ink not soluble in the developing solution for the photosensitive resin composition should be used to thereby obtain duplicate printing plates from a master plate. To aqueous developer or alkali developer processable negative type photosensitive resin compositions there may be applied an oleophilic offset Ink for general use. If the ink composition is capable of transmitting light that is active for the photosensitive resin composition, the ink composition, by applying a post-exposure after development, permits the production of duplicate printing plates capable of withstanding the printing of a much larger number of copies. As the resin layer in the present invention, conventional positive type photosensitive resin compositions may also be used. Therefore, commonly used lithographic positive type P.S. plates may be employed as the printing plate of the present invention having a resin layer on the printing plate material. In this case, the photosensitive resin composition should be exposed to light that is active therefor before development.

The resin layer of the present invention may be a single layer or two or more layers, and also may be either photosensitive or non-photosensitive. These duplicate plates may be made capable of having an even longer press life by being subjected to a burning treatment after the resist formation. Particularly, a duplicate plate having a matrix-structured resin layer thereon tends to have significantly improved press life if it is subjected to a thermal treatment. The temperature of such a thermal treatment, although dependent on the composition of the resin layer, is preferably from 150°C to 300°C, and a plate having a matrix-structured resin layer should be subjected to a thermal treatment at a temperature of more than that at which the matrix particles become molten.

If the resin layer is excessively thick, then some of the hilight dots in the image area may be lost, so that the image deteriorates, whereas if the layer is too thin, then the effectiveness of the resin layer is reduced. When taking into account the protectability, press life, relief strength, developability, etc of the printing plate, the preferred range of the thickness if generally from 0.1μ to 25μ, more preferably from 0.5μ to 10μ.

The printing ink for use in the present invention, when it is provided on the resin layer, should be insoluble in a solvent for use in the removal of the resin layer, and should adhere strongly to the resin layer. Such a printing ink may be selected from among those inks whose ink layer on the resin layer has a resisting effect at the time of dissolving the resin layer by a solvent; hence, oxidation polymerization hardening inks, photo-hardening type inks and thermally hardening type inks, for example may be used. If desired, an Ink whose composition has a strong adherence with the resin layer and has a coefficient of solubility similar to that of the resin of the resin layer, is used in combination with the resin whose crystalline nature is similar to that of

the ink. Generally, an oily ink is used for duplicate printing plates where the resin layer is removed in an aqueous developing solution.

The formation of an image using an ink on the printing plate having a resin layer thereon of the present invention may be carried out from a master plate using such known printing procedures as offset printing, relief printing, typing, screen process printing, deep-etch printing or ink-jet printing.

After the printing, the resin layer in the non-image area is dissolved and removed by a solvent (hereinafter also called "development") to obtain a printing plate. After the printing, although it is desirable to develop by hardening the ink, the following selection of materials may be used, for example, as a printing ink, an oily offset ink such as of the oxidation polymerization hardening type, photo-hardening type or thermally hardening type can be used to make a printing on a alkali-soluble resin-coated aluminum plate, which is then, in an unhardened condition, developed in a bath tray filled with an alkali aqueous solution, thus obtaining a printing plate. Upon completion of the development, the printing plate thus obtained may be applied to a printing press to carry out a printing operation. Generally, the use of an oily ink and water or alkali aqueous solution as a developer is most suitable for the production of printing plates.

As solvents for use in dissolving and removing the resin layer, if they are capable of removing only the non-image area without dissolving the inked layer in the image area, water or various solvents can be used. For example γ-butylolactone which comprises at least one of glycerol, water and phosphoric acid can be used. From the safety and health points of view, it is desirable to use an aqueous solvent such as an inorganic alkali solution containing, for example, sodium silicate, sodium carbonate, sodium hydroxide, potassium silicate, potassium hydroxide, lithium hydroxide, sodium diphosphate, sodium triphosphate, ammonium diphosphate, ammonium triphosphate or sodium metasilicate. To the alkali solution there may be added singly or in a combination surface active agents or solvents such as cyclohexanone, benzyl alcohol, cyclopentanone, methyl cellosolve (ethylene glycol monomethyl ether), methyl cellosolve acetate, methyl cellosolve acetate, carbitol, dioxane, phenyl cellosolve, ethyl cellosolve or ethyl cellosolve acetate. Solvents to be used in the present invention are not limited to these solvents but include any others which do not dissolve the inked layer but are capable of removing the non-image areas of the resin layer.

In addition, the printing plate materials provided on the surface thereof with the resin layer possesses excellent storability as compared to known printing plate materials not having such resin layers.

The following Examples further illustrate the present invention.

Example 1

In a nitrogen gas flow, to 100 ml of dioxane were added 0.6 mol of styrene, 0.4 mol of methacrylic acid and 0.001 mol of azo-bis-isobutylonitrile, and the mixture was reacted at the temperature of 65°C over a period of 41 hours. The resulting solution was put into a large amount of water to thereby obtain a precipitated polymer. The polymer was extracted by filtration and then dried. To the polymer was added 3% by weight of crystal violet and the mixture was dissolved in methyl cellosolve. Separately, a 0.3 mm thick aluminum plate was subjected to an electrolytic polishing treatment, and then to anodic oxidation, thereby preparing a printing plate material. On the aluminum plate the foregoing resin liquid was coated by means of a rotary coating machine so that the thickness of the resin layer becomes about 1μ. After drying, the resulting printing plate was printed thereon with an image from a master plate using an offset proof press. The ink used was Toyo King Ultra 70, manufactured by Toyo Ink Co., Ltd. After the printed ink had dried, the plate was subjected to a tray development with a 0.5% aqueous sodium metasilicate solution for 60 seconds at the temperature of 25°C, whereby a non-image-area-removed printing plate was obtained. The printing plate thus obtained was applied to a printing press to carry out a printing operation; there were produced up to 150,000 copies with excellent image reproduction with no trouble.

Example 2

An aluminum plate prepared in the same manner as in Example 1 was coated thereon with m-cresol formaldehyde novolak resin dissolved into methanol by means of a rotary coater so that the resin coated layer is about 2μ thick. After drying, the resulting printing plate material was printed thereon with an image from a master plate by use of an offset proof press. The ink used was Fresh Dry, manufactured by Toyo Ink Co., Ltd. After the printing, the plate material was exposed for three minutes to a 2KW high pressure mercury vapor lamp, and then developed in a 4% aqueous sodium metasilicate solution bath for 60 seconds at 25°C to thereby obtain a printing plate. The printing plate thus produced was applied to a printing press to carry out a printing operation; the plate was found to provide excellent sensitization with good oleophilicity, thus giving up to 80,000 printed copies having excellent reproduction with no trouble.

Example 3

An aluminum plate prepared in the same manner as in Example 1 was coated thereon with a coating liquid comprising a p-hydroxy-phenyl methacrylamide—methyl methacrylate—acrylonitrile—methacrylic acid copolymer (molar ratio: 2:4:3:1) dissolved in methyl cellosolve by means of a rotary coater so that the coated layer is in the thickness of about 1μ. In a similar manner to that of Example 2, from a master plate

a duplicate plate was produced. The resulting plate was developed for 60 seconds in a 3.5% aqueous sodium metasilicate solution at 25°C to thereby obtain a printing plate, which was then applied to a printing press, thereby printing 180,000 copies. No harm was found in the relief of the printing plate.

Example 4

An aluminum plate prepared in the same manner as in Example 1 was coated by means of a wire bar with a dispersion liquid of Gosenol GL-05 (polyvinyl alcohol, manufactured by Nippon Synthetic Industry Co., Ltd.) and Copolene L-4000 (ethylene-vinyl acetate copolymer, manufactured by Asahi Dow Co., Ltd.) in the proportion by weight of 3:4 dispersed in water. The coated product was dried by ventilation at a temperature of 50°C. The coated layer was about 2μ thick. On the resulting printing plate an image from a master was printed by an offset proof press. The ink used was Diatone AK-SSP, manufactured by Sakata Shokai Co., Ltd. This was developed in running water to remove the non-image area, and was subsequently subjected to a thermal treatment for three minutes at 200°C, whereby a printing plate was produced. The thus produced printing plate was applied to a printing press to thereby obtain satisfactorily printed 150,000 copies; no harm was found to the image on the printing plate.

Example 5

An aluminum plate prepared in the same manner as in Example 1 was coated by means of a wire bar with a dispersion liquid prepared by dispersing over a period of 24 hours using a ball mill a mixture of 5 parts by weight of mcresol formaldehyde novolak resin with 1 part by weight of copper phthalocyanine into a methyl cellosolve solution so that the dry thickness of the coated layer becomes 3μ. On the resulting product an image from a master plate was printed by an offset proof press. The ink used was Toyo King Ultra 70, manufactured by Toyo Ink Co., Ltd. After the printed ink dried, the product was developed for 20 seconds in a 4% aqueous sodium metasilicate solution at 20°C to thereby obtain a printing plate, which was then applied to a printing press to produce 150,000 printed copies. After the printing, no harm was found to the image of the printing plate.

Example 6

An aluminum plate prepared in the same manner as in Example 1 was coated thereon with a liquid of 1,2-naphthoquinone-diazide-sulfonic acid ester of m-cresol-formaldehyde-novolak resin in the amount of 20% by weight to that of the resin in Example 2 dissolved in methanol so that the coated layer is of thickness about 2μ. After drying, an image from a master plate was printed by an offset proof press on the resulting duplicate plate. The ink used was Fresh Dry, manufactured by Toyo Ink Co., Ltd. After the printing, it was exposed for three minutes to a 2KW high pressure mercury vapor lamp light, and then developed for 60 seconds in a 4% aqueous sodium metasilicate solution at 25°C to thereby obtain a processed duplicate plate, which was then applied to a printing press to make 100,000 copy prints; no harm was found to the image of the printing plate.

Example 7

An aluminum plate prepared in the same manner as in Example 1 was coated by means of a rotary coater with a liquid of a condensate of 4-diazo-4'-phenylamino hexafluorophosphate with formaldehyde in the amount of 8% by weight to that of the resin in Example 3 dissolved in methyl cellosolve solvent. The coated layer thickness was about 1μ. After drying, the resulting product was printed thereon with an image from a master plate by means of an offset proof press. The ink used this time was one produced from a mixture of 60 parts by weight of linseed oil aliphatic acid, 30 parts by weight of trimethylol propane and 10 parts by weight of phthalic anhydride reacted for a period of 4 hours in a nitrogen gas flow at the temperature of 220°C, to which reaction product, after cooling down to 90°C, were added 15 parts by weight of benzene and 10 parts by weight of acrylic acid to react while stirring for a period of three hours, the viscosity of which reaction product was then controlled by the addition of a linseed oil varnish to 700 poise, to which were then added 3% by weight of benzoin methyl ether and 3% by weight of Michler's ketone. After the printing, the duplicate plate was developed in a 3.5% aqueous sodium metasilicate solution to remove the non-image area thereof, and further was exposed to a 2KW high pressure mercury vapor lamp light for three minutes to thereby obtain a printing plate, which was then applied to a printing press, thereby making satisfactory 180,000 copy prints. No harm was found to the image of the printing plate.

Claims

1. A method for the production of a printing plate which comprises forming a printing ink image on a resin layer provided on a printing plate material, and dissolving the resin layer with a solvent therefor which does not dissolve the inked image.

2. A method according to claim 1 wherein the image is produced using a master printing plate.

3. A method according to claim 1 or 2 wherein the resin layer is formed on aluminium.

4. A method according to any one of claims 1 to 3 wherein the resin layer is of an acrylic resin.

5. A method according to any one of the preceding claims wherein the printing plate provided with the printing ink image is a lithographic negative type presensitized plate and the ink is one which is not soluble in the developing solution for the presensitized plate.

6. A method according to claim 5 wherein the

developing solution is aqueous and the ink is oleophilic.

7. A method according to any one of the preceding claims wherein the ink is an oxidation polymerisation hardening ink. A photo-hardening ink or a thermally hardening ink.

8. A method according to claim 1 substantially as described in any one of Examples 1 to 7.

9. A printing plate whenever produced by a method as claimed in any one of the preceding claims.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1982. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.